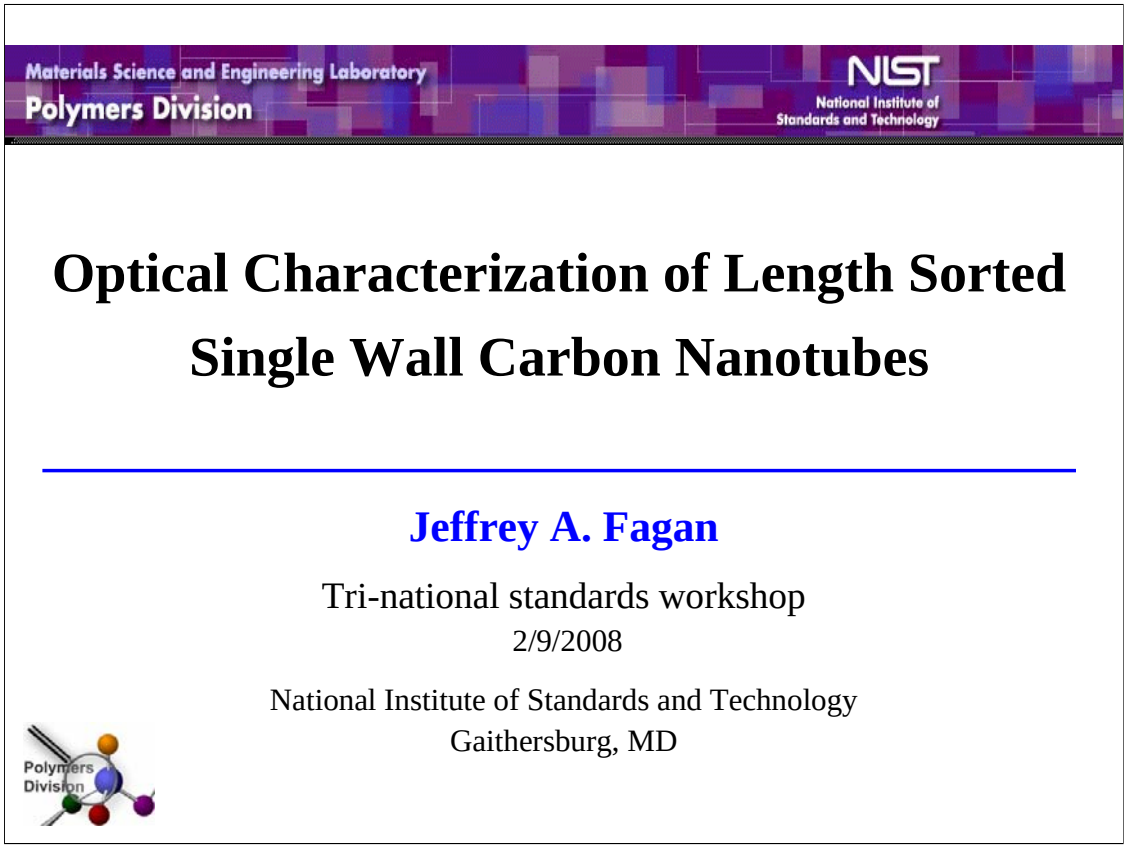
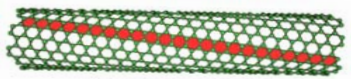


Dr. Jeffrey Fagan's presentation from the Tri-national standards workshop February 9th 2008.

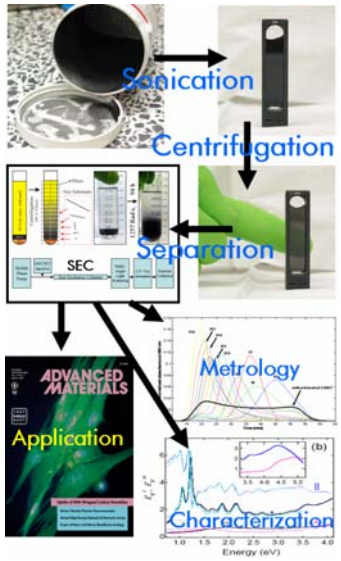
Certain commercial equipment, instruments, or materials (or suppliers, or software, ...) are identified in this presentation to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

In all figures with symbols, error bars representing one standard deviation are shown only when larger than the symbol; in figures with lines error bars are commensurate with indicated scatter.

NIST SWCNT Competence



2008 is the 3rd year of the NIST SWCNT competence project.



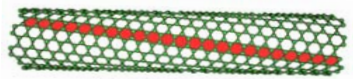
Our strategy of purification and separation allows for metrology improvement and characterization by length and type.

Collaborative team with complementary skills in polymer characterization, soft matter and colloidal physics, and optical characterization.

Approaching a dozen publications in the last 3 years in high impact journals including JACS, PRL, J. Phys Chem B, J. Phys Chem C., Advanced Materials, and Analytical Chemistry.

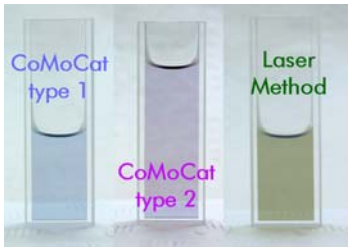
Our group is in the 3rd year of a funded initiative. Our mission is to develop methods to produce well-characterized fractions of carbon nanotube suspensions with measured parameters (length, type, charge, concentration and impurities) and to utilize them for the development of measurement methodologies, underlying emerging applications, characterization of intrinsic properties and to address EHS concerns. We have a strong team and are producing significant products.

NIST SWCNT Competence



The NIST SWCNT project has been highly productive.

Examples of recent publications

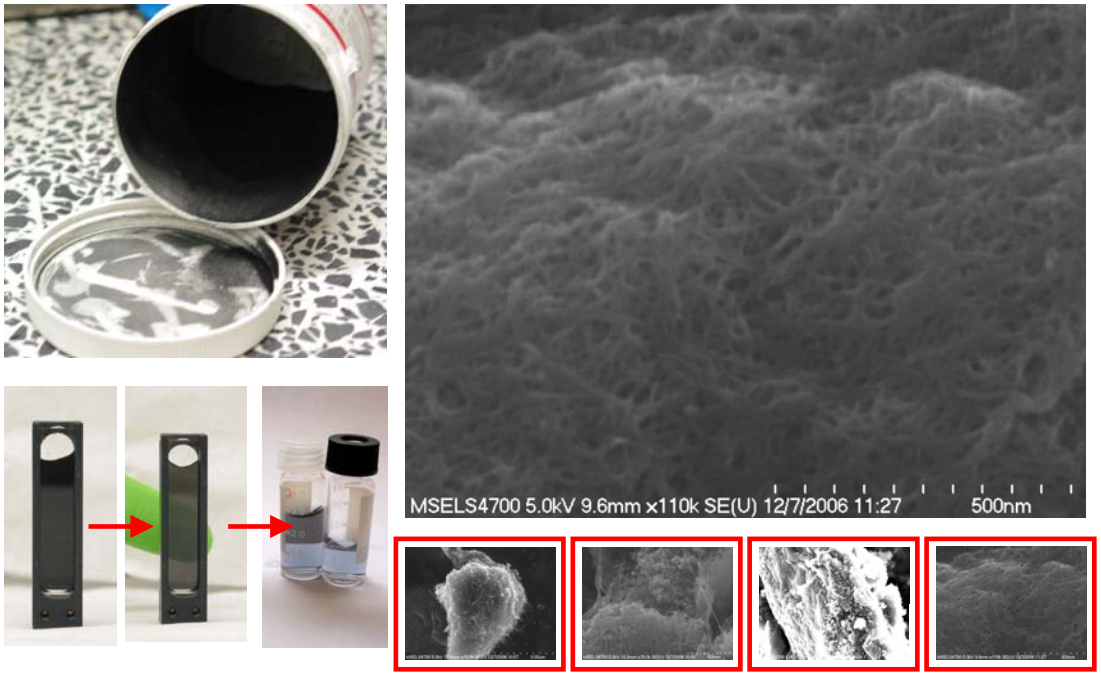


Long SWCNTs from different soots.

Ongoing work, exploiting our purified materials, in optical characterization, biological identification, patterning and templated growth, metrology improvements and further optimization of the separation processes.

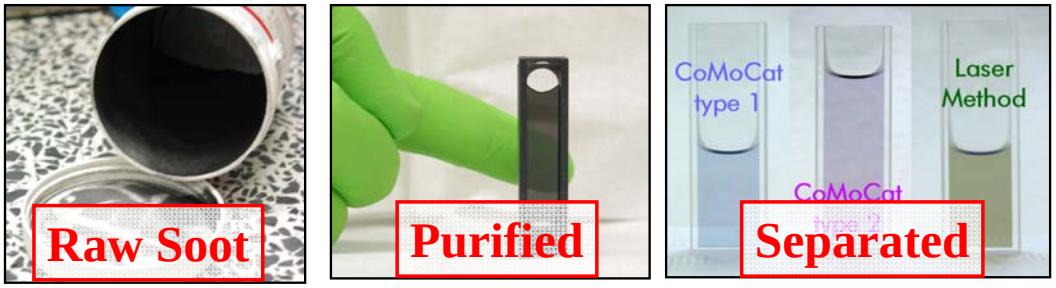
Our group is in the 3rd year of a funded initiative. Our mission is to develop methods to produce well-characterized fractions of carbon nanotube suspensions with measured parameters (length, type, charge, concentration and impurities) and to utilize them for the development of measurement methodologies, underlying emerging applications, characterization of intrinsic properties and to address EHS concerns. We have a strong team and are producing significant products.

What should be our goal for an SRM?



A key question is what should be the goal for the SRM. Should it be a reference for as manufactured soot (leftmost two lower SEM images), a purified liquid or dried soot with the contaminants removed (sediment from the initial centrifugation at 21 000 *g in the 3rd pict, the supernatant from the initial centrifugation at 21 000 *g in the large view and last small SEM), or a highly purified and separated material (blue liquid). The initial soot is measured to be (55 to 60) % SWCNTs by mass, by both TGA and UV-Vis-NIR absorption changes, and the supernatant approximately 90 % SWCNTs, a separated material would be roughly 100 % pure and be sorted by a specific property such as SWCNT length.

What should be our goal for an SRM?

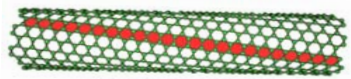


- In fact, there appears to be a need for all three grades / types of material

- Our focus is on the third of these, producing an aqueous phase length sorted standard.

The raw soot is most comparable to the material used by industrial producers, dispersed and purified material (having removed most of the non-SWCNT material) is probably closest to the material that will be used by high volume industrial consumers, and highly purified and separated materials are the best exemplifiers of intrinsic properties and the material that will be used for high technology applications. There are likely markets for all three types of materials. My focus is on the highly purified and separated SWCNTs.

Why Length Sort?:



The length of the nanotube is its most obvious and second most important characteristic!

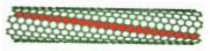
Tube length affects the optical properties, percolation lengths for electrical, thermal and mechanical properties, alignability processing variables such as viscosity, and the toxicity of the nanotubes.

Short 

Long

Why length sort? The length of the nanotube is extraordinarily important in dictating the expected properties of the material, as well as its processability. We have found that the length directly impacts the key optical and electrical properties of the SWCNTs, as well as other factors such as the cellular uptake rates of the dispersed nanoparticles. Since many properties are directly affected by length it is important to perform the separation such that these effects can be measured.

Separating Carbon Nanotubes:



Several techniques have been used to sort nanotubes by tube length.

Method Comparison

M. Zheng et al. at Dupont

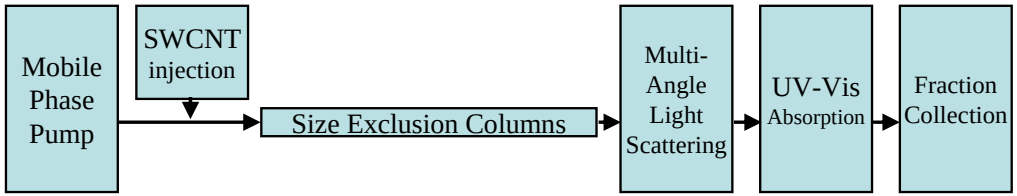
Fagan et al. at NIST

Method	Analytical / Preparative	Batch Size	On-Line Analysis	Mw / Mn	SWNT size (nm)	Comments
SEC	A + P	200 (2000) µg	Photodiode array, MALS, Viscosity, Refractive Index	1.5 to 1.1	50 to 500	Best on-line measurements. Short SWNTS contaminated with long. DNA dispersions only. Not robust.
FFF	A	20 µg			20 to >1000	Analytical only. Best separations. Many dispersion types. Robust.
UC	P	20000 µg	none	< 1.5	20 to >2000	Large quantities. Many dispersion types. Broad size range. Very Robust.
SWNT fracture	P	> 10000 µg	none	> 1.5	50 to 1000	Very broad distributions. Damaged SWNTs. Large quantities. Many dispersion types. Can only shorten.
Gel EP	A	< 20 µg	none			Very small quantities. Only certain dispersions

Several techniques have been proposed/developed for length separation of SWCNTs, however none has been commercialized due to either the extremely high cost (> ~ $50 / mg for SEC), unsuitable methodology for scale-up, or the poor performance of the separation. For the purposes of this talk, size exclusion chromatography, developed by Ming Zheng and others at DuPont, and using DNA dispersed SWCNTs, and ultracentrifugation length separation, developed at NIST and using deoxycholate dispersed SWCNTs, are of primary interest.

Size Exclusion Chromatography:

Chromatographic Separation



Dr. Barry Bauer

Separation by Hydrodynamic Radius

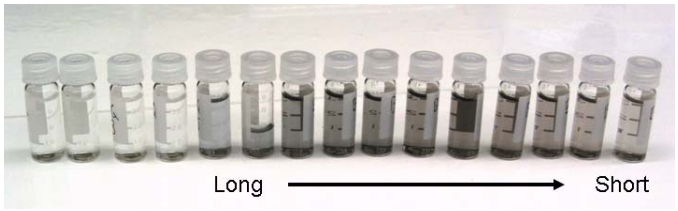
- large objects are removed by a 0.45 μm prefilter
- easy to perform multiple identical separations
- Multi-angle light scattering and UV-Visible light absorption performed online.
- Requires DNA dispersion

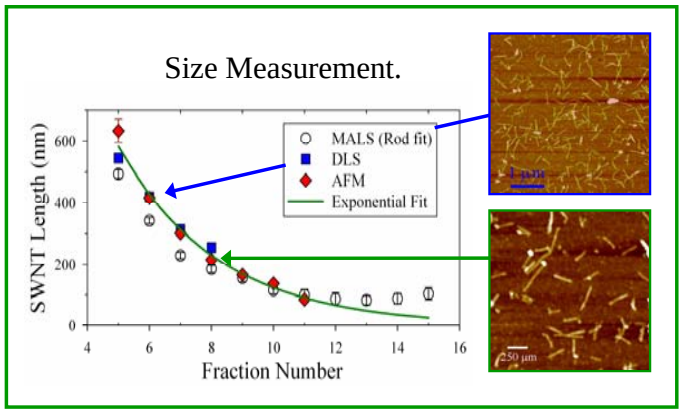
Results published in Fagan et al. *JACS* **2007**, 129, 10607-10612.

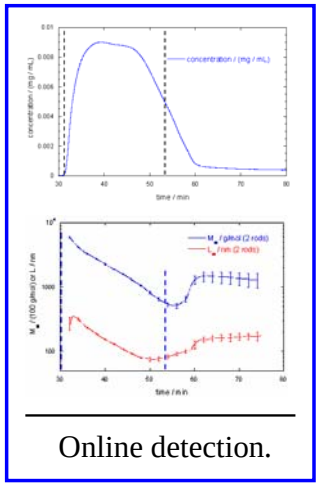
The first technique that we used to separate the nanotubes by length was size exclusion chromatography (SEC). In SEC a plug of nanotube solution is injected into a column containing porous packing with various size pores, into which the SWCNTs will fractionate based upon the size of the nanotube. As the solution moves through the column smaller tubes spend progressively more time within these pore volumes, hence longer SWCNTs move faster through the column, and elute earlier. For DNA wrapped SWCNTs, this procedure was developed by Zheng *et al.* at DuPont [Huang, X. Y.; McLean, R. S.; Zheng, M. *Anal. Chem.* **2005**, *77*, 6225., Zheng, M.; Jagota, A.; Semke, E.D.; Diner, B.A.; McLean, R.S.; Lustig, S.R.; Richardson,R.E.; Tassi, N.G. *Nat. Mater.* **2003**, *2*, 338.].

In our setup Dr. Barry Bauer added online multi-angle light scattering and UV-Vis absorption detection before the fraction collector to improve the analytical measurement. All of our SEC results are contained in a recent JACS article [Fagan, J. A.; Simpson, J. R.; Bauer, B. J.; Lacerda, S.; Becker, M. L.; Migler, K. B.; Hight Walker, A. R.; Hobbie, E. K. *J. AM. CHEM. SOC.* **2007**, 129, 10607-10612], Results and details of the online light scattering characterization are in *J. Phys Chem C.* [Bauer, B.J.; Fagan, J.A.; Hobbie, E.K.; Chun,J.; Bajpai, V. *J. Phys. Chem. C.* **2008**.].

Size Exclusion Chromatography:



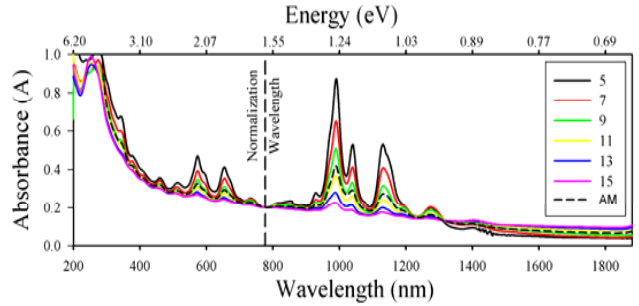




Results published in
Fagan et al. *JACS* **2007**, 129, 10607-10612.

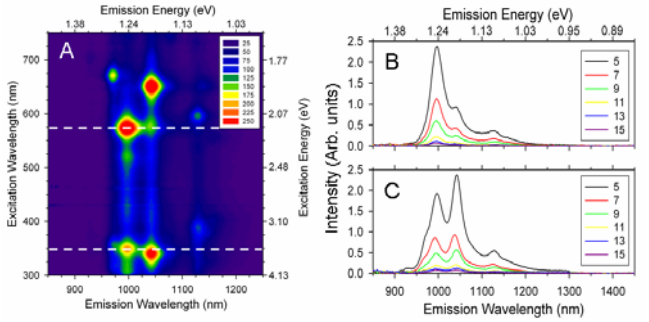
A set of fractions from the SEC separation is shown. The longest SWCNTs begin eluting in our fifth fraction, indicating the exclusion limit of the column, and get progressively shorter through fraction 15, at which point DNA begins to elute and the SWCNT concentration drops sharply. Some of the online detection results, such as multi-angle light scattering are shown to the right. A comparison of some of the measured size results from different techniques for the set of fractions is shown below.

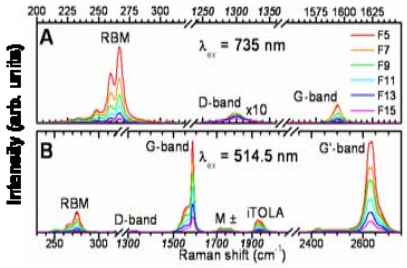
Size Exclusion Chromatography:



Key finding:

Optical properties ***increase*** with SWCNT length!



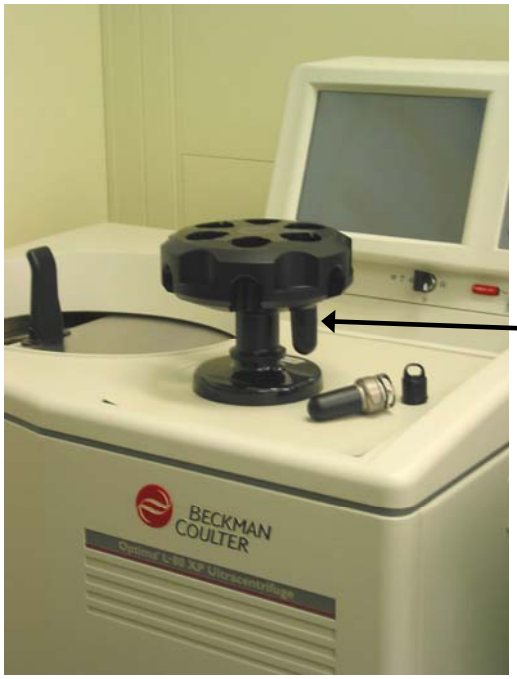


Results published in
Fagan et al. *JACS* **2007**, 129, 10607-10612.

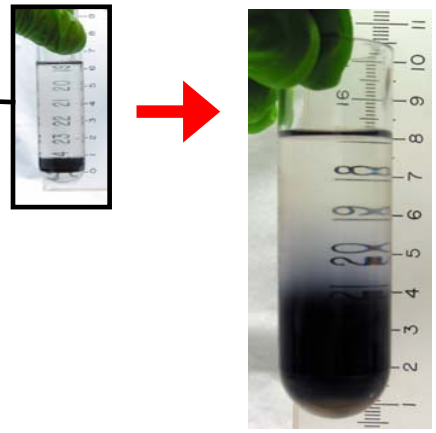
The key finding from the SEC work was the length dependence of the optical transition strengths.

The increase in peak to baseline ratio of the absorbance with SWCNT length occurs regardless of the wavelength chosen for concentration normalization. This finding can also not be explained away by purity arguments unless the injection concentration was less than 13 % pure using only the SEC results; the estimated value (backed up by SEM, TEM, and TGA of the raw soot and the dispersed material) is (90 to 95) % purity of SWCNTs in the injected liquid. The purity value would have to be even lower < 4% using results measured using centrifugation sorting that will be described later in the talk. Of note is that the peak absorption in the longest fractions approaches the size of the Pi-plasmon absorption feature. Generally even the absorption spectra of the as produced (sonicated, 2 h centrifuged, labelled in this figure as AM) is substantially better than most spectra reported in the literature. This finding also extends to the intrinsic NIR fluorescence of the Nanotubes (a PL map of CoMoCat material and slices at 573 and 348 nm are shown), and to the resonant Raman scattering. These results are published in Fagan et al. *JACS* **2007**, 129, 10607-10612.

Length Separation by Centrifugation



Length fractions can also be produced through centrifugation

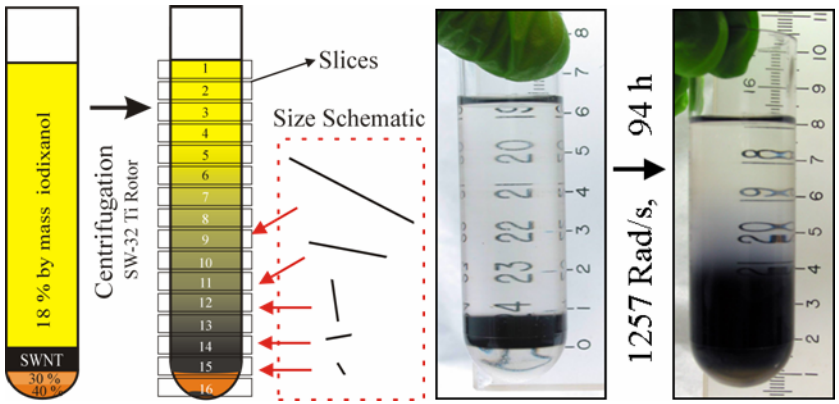


1257 rad/s , 94 h

The second technique used for length fractionation in this work was performed using centrifugation of the SWCNTs in a dense liquid. Separation is driven by the difference in the transient motion of SWCNTs in a dense liquid due to a difference in scaling of the buoyancy and frictional forces with the aspect ratio of a SWCNT.

A paper detailing the initial demonstration of separation by this method has been accepted in *Advanced Materials.*

Length Separation by Centrifugation



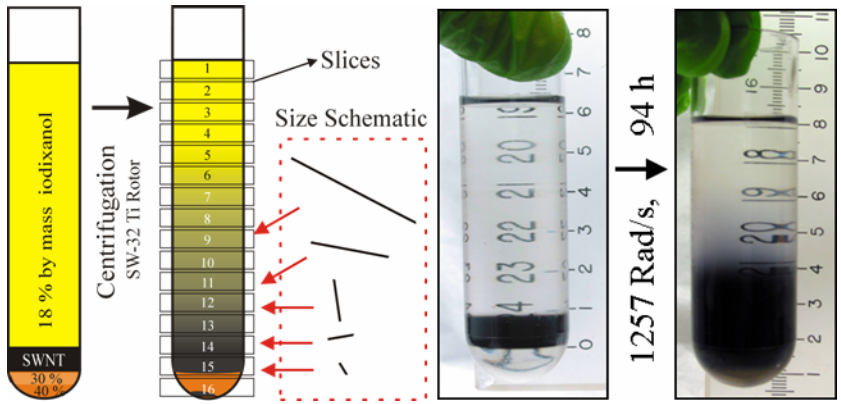
The buoyancy force on a rod $F_{buoyancy} = \pi r^2 \ell * \left(\rho_s - \rho_{SWNT,i}\right) * G$

Scales with length differently than the friction coefficient.

$$f_{\parallel} \propto \frac{\pi \eta \ell}{\gamma}\left(\frac{1+0.307/\gamma}{1-0.5/\gamma}+\frac{0.426}{\gamma^2}\right),\ f_{\perp} \propto \frac{\pi \eta \ell}{\gamma}\left(\frac{1+0.307/\gamma}{1+0.5/\gamma}+\frac{0.119}{\gamma^2}\right),\ \gamma = \ln(\ell/r)$$

The separation can be described mathematically either through a Flux (Nernst-Planck formulation) or in a single particle velocity sense. The difference in the scaling of the friction factor and the buoyancy force on the rod with aspect ratio results in the prediction that longer SWCNTs will travel with a greater velocity in response to an applied centripetal acceleration.

Length Separation by Centrifugation



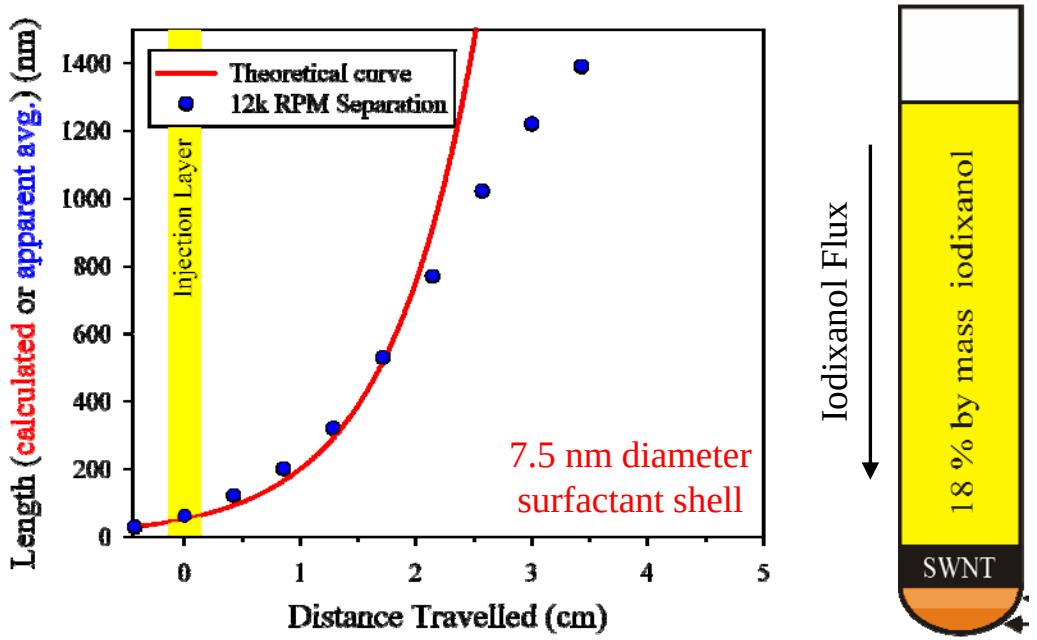
The flux is thus $N_i = c_i F_{buoyancy} / f_i - D_i \nabla c_i$ with $D_i = k_B T / f_i$ where f_i is the friction coeff.

Leading to a length dependent velocity of the SWNTs, with longer tubes moving faster.

$$N_i(\ell) \propto c_i \frac{(\rho_s - \rho_{SWCNT,i}) G r^2}{\eta} \frac{\gamma^4 + 0.614\gamma^3 + 0.3883\gamma^2 - 0.3943\gamma}{2\gamma^3 + 0.615\gamma^2 + 0.044\gamma - 0.1535}$$

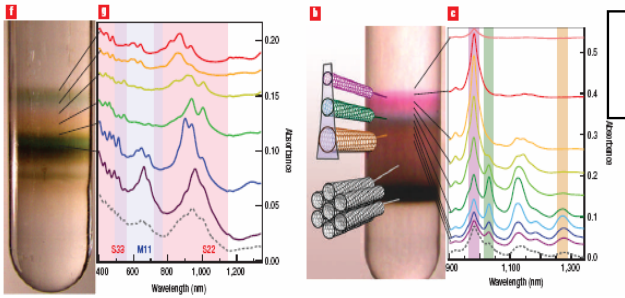
The separation can be described mathematically either through a Flux (Nernst-Planck formulation) or in a single particle velocity sense. The difference in the scaling of the friction factor and the buoyancy force on the rod with aspect ratio results in the prediction that longer SWCNTs will travel with a greater velocity in response to an applied centripetal acceleration.

Length Separation by Centrifugation



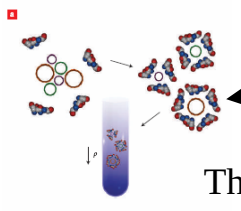
Taking into account the motion of the iodixanol polymer, the simple theory does a good job of explaining the separation.

Chirality (Diameter) Separation by Centrifugation



From Arnold *et. al.* Nature Nanotechnology, 1, 60-65, 2006

Demonstrated chirality separation of SWCNTs by exploiting differences in the specific gravities of the SWCNT-Surfactant shell complexes.



Different diameter SWCNTs have different densities in this surfactant solution.

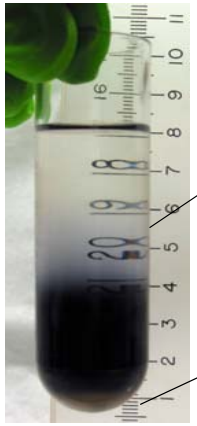
The difference is that their separation is achieved as the SWCNTs go to their ***equilibrium*** positions.

They exploit $\Delta\rho_{SWNT} = \langle \rho_{SWNT} \rangle - \rho_{SWNT,i}$

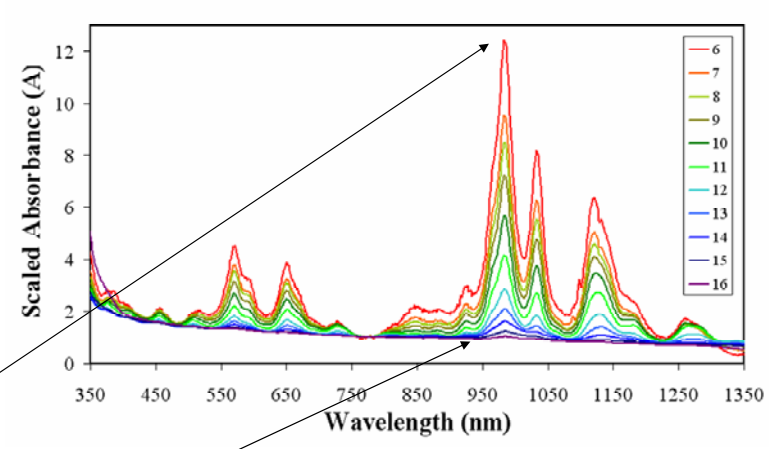
Rather than $\Delta\rho = \rho_s - |\rho_{SWNT}| >> \Delta\rho_{SWNT} = |\rho_{SWNT}| - \rho_{SWNT,i}$

If you are familiar with recent literature you may notice that our technique appears similar to the chirality separation demonstrated by Arnold et al. in [*Nature Nanotechnology*, 1, 60-65, **2006**]. The key difference is that we utilize the relative velocities of SWCNTs when the difference in buoyancy force on any given SWCNT is minimal compared to a large difference between any surfactant encapsulated SWCNT and the medium, and thus rely on ***transient*** processes to separate the SWCNTs by length, whereas Arnold et al exploit the differences in densities of the different types of SWCNTs, and attempt to drive the SWCNTs to their ***equilibrium*** positions within a gradient.

Length Separation by Centrifugation



1257 rad/s, 94 h

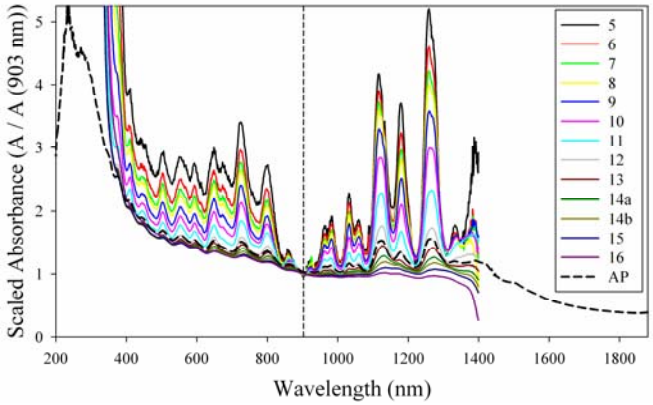


Material that travels the farthest, i.e., the longest SWCNTs, has the largest optical transitions, with the same length dependence as observed in the SEC

Fractions collected after the 1257 rad/s, 94 h separation show substantial and monotonic increases in peak to baseline ratio, without evidence of chirality separation, with the distance travelled by the SWCNTs. Note the purplish color of the larger fractions due to the increase in relative size of the E22 features above the baseline absorption.

Length Separation by Centrifugation

An example of spectra from a HiPCO separation. We have also separated EA and Laser type SWCNTs

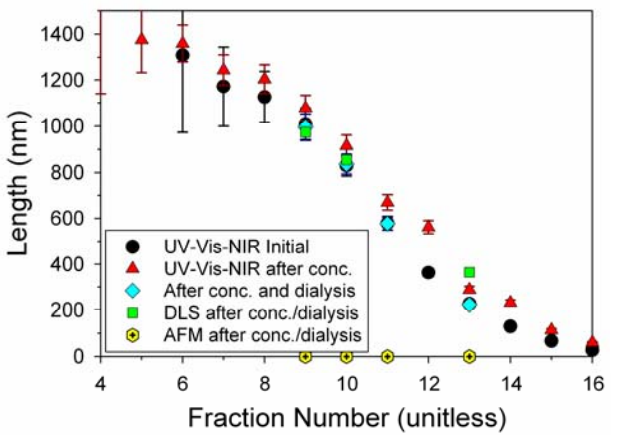


- As with CoMoCat material, the transition peaks increase at the same rate, indicating no chirality separation.
- Same parameters used for the separation; slight modification could improve the process, especially for EA or laser type SWCNTs

As in the SEC, we also have run other sources of SWCNT material through the centrifugation separation. Above is a set of spectra from the separation of a HiPCO process sample. The unsorted solution is the dashed line. Deviation of the separated sample spectra below 400 nm and above 1300 nm are due to imperfect subtraction error of the (large) iodixanol solution absorption. Note that the size of the Pi-Plasmon peak is expected to be nearly constant across the fractions, indicating that several chirality features are approaching that size in the longest fractions. Also note that all of the chiralities are increasing at the same relative rate, this is not the effect of chirality separation.

Length Separation by Centrifugation

The average length and distribution of lengths in each fraction can be measured through a variety of techniques including field flow fractionation (FFF), atomic force microscopy (AFM), dynamic light scattering (DLS), multi-angle static light scattering (MALS), and optical calibration

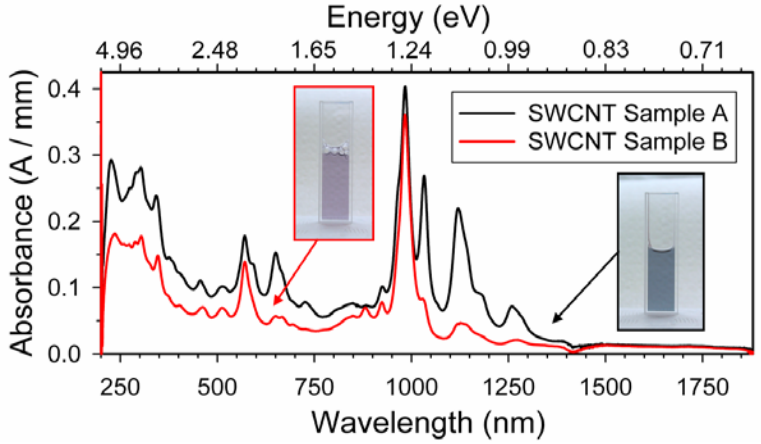


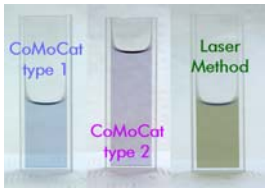
Lengths from various techniques

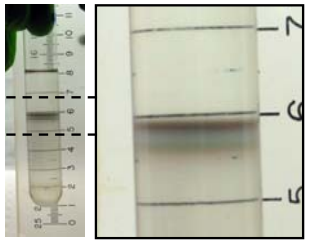
Separation at 1257 Rad/s, 94 h, 15 C

We can measure the lengths through a variety of techniques, field flow fractionation (FFF), atomic force microscopy (AFM), dynamic light scattering (DLS), multi-angle static light scattering (MALS), or optical calibration.

Length Separation by Centrifugation





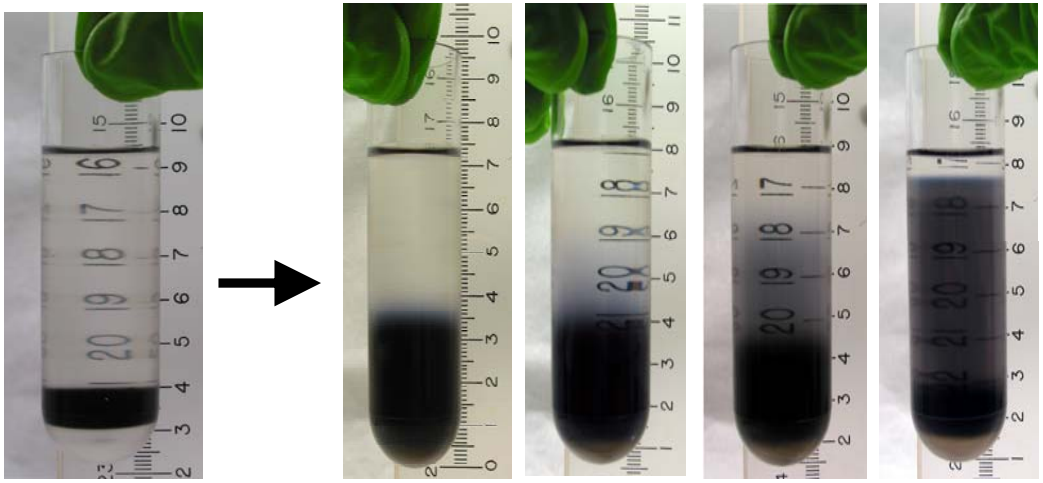


- The longest fractions have dramatically superior optical properties.
  - These fractions become colored due to the increased selective removal of certain wavelengths.
  - Chirality separation further increases the intensity of color.

Pictures and spectra of some long fractions, and to the right an example of chirality separation of length sorted HiPCo material.

The longest fractions become colored due to the increase in relative size of the optical transitions in the visible wavelength range to the broad underlying background absorbance. Note that the E11 features substantially exceed the absorbance in the pi-plasmon region. These samples will allow for new optical property based investigations.

Length Separation by Centrifugation

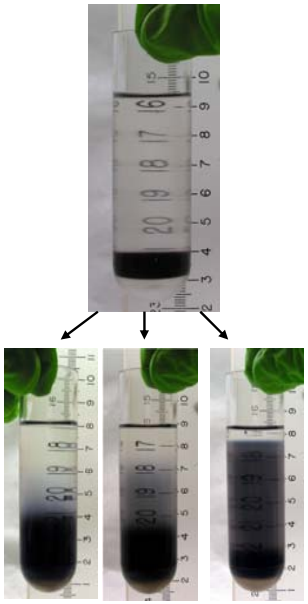


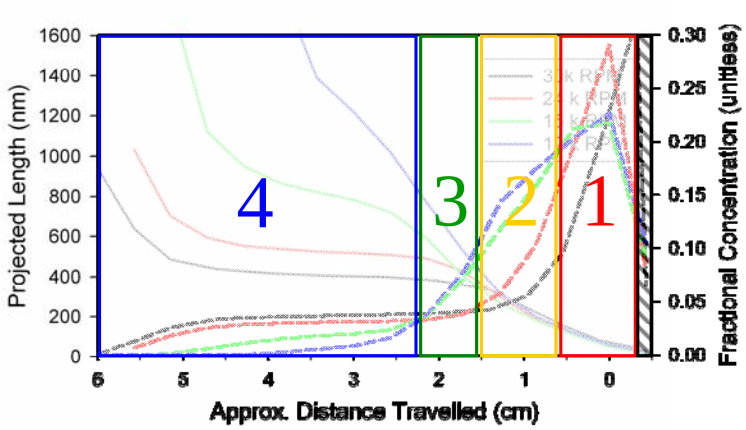
Initial	785 rad/s 240 h	1257 rad/s 94 h	1570 rad/s 60 h	3141 rad/s 15 h

Identical integrated force in each experiment: Different results

This is not to say that everything is easy and perfect with length separation by UC. For instance here are shown pictures of the result from running the separation for identical total integrated force on the liquid, but with different rotational rates. Slower, longer separations proceed closely with the theoretical predictions. Faster separations seems to induce additional effects that induce mixing of the shorter SWCNTs into long SWCNT fractions. The appropriate modulation of parameters (not discussed in this talk) allows us to minimize these effects.

Length Separation by Centrifugation





Avg. Lengths = ~ 125 nm
~ 250 nm
~ 350 nm

Using the UV-Vis-NIR length projection the length versus distance curves can be plotted. The 1257 rad/s separation most closely follows the theoretical form. Convincingly, normalization at 775 nm is demonstrated to be a good indicator of concentration by these curves. Integration of the length in each separation with the measured concentration in each fraction yields identical values for the average length of the initial identical injections. If the normalization were not a good indicator of concentration, then these curves would not reach equivalent summed values.

The curve for 1257 rad/s is consistent with a buoyant radius (using the equilibrium value for the nanotube plus micelle density) of ≈ 3.5 nm, combined with a towards the bottom of the tube directed drag due to the sedimentation of the density liquid polymer.

Overlaying regions onto this concentration curve displays the sort of range of length fractions that could be achieved for an SRM.

Current Stage of Process:

1. Identifying a common material source for the multiple projected NIST SWCNT RM/SRM materials.
2. Determining the most effective measurement methods and road mapping potential characterization.
3. Demonstrating the stability / reproducibility of measurable parameters.
4. Projected production / certification in FY 2009

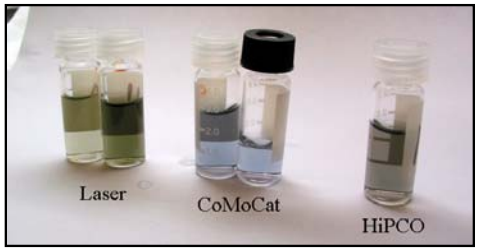
Conclusions.

Directions:

- Multiple grades of SWCNT reference material will be valuable to different communities.
- The availability of purified samples should allow for unambiguous EHS assessments, intrinsic property characterization and technology development.
- In a purified sample, SCWNT length is an important parameter that can be controlled.
- NIST is seeking input as to the most value in a SRM

Conclusions.

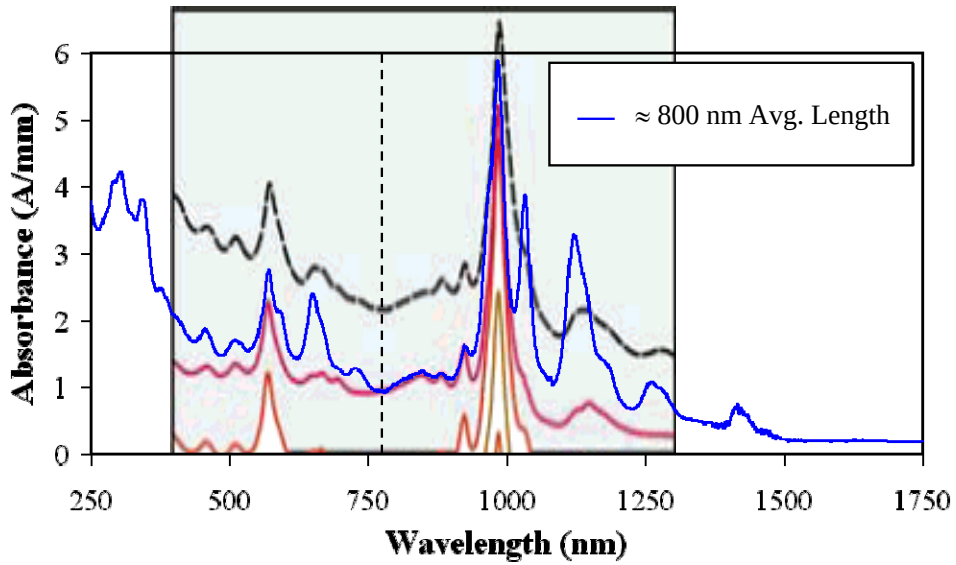
Acknowledgments:



Many people contributed to this work across MSEL, Physics Lab, and NCNR.

Many people contributed to this work across MSEL, Physics Lab, and NCNR. Pictures of some of these people are shown.

Length Separation by Centrifugation:



Chirality purified figure from Crochet *et al. J. Am. Chem. Soc.* **2007**

The increase in absorption is so significant that longer SWCNT solutions that are not chirality separated can have larger transition sizes than chirality sorted material. Shown is a comparison to spectra of heavily enriched (6,5) SWCNTs by Crochet *et al. J. Am. Chem. Soc.* **2007** (magenta line) to an chirality unpurified but approximately 800 nm long fraction (that has been dialyzed to remove the iodixanol). Note that the blue curve has a larger peak to baseline ratio at 984 nm, despite being composed of only approximately 20 % (6,5) SWCNTs.